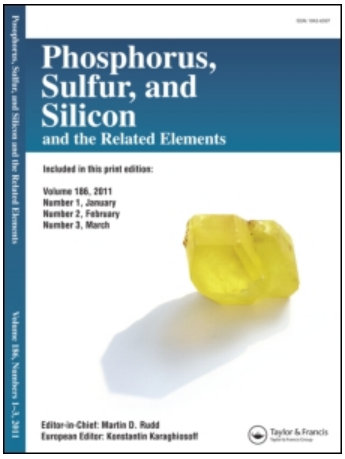

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SULFUR CHEMISTRY IN THE NEXT FEW DECADES—WOULD SEVERAL UNSOLVED PROBLEMS BE CLARIFIED?

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SULFUR CHEMISTRY IN THE NEXT FEW DECADES--- WOULD SEVERAL UNSOLVED PROBLEMS BE CLARIFIED?

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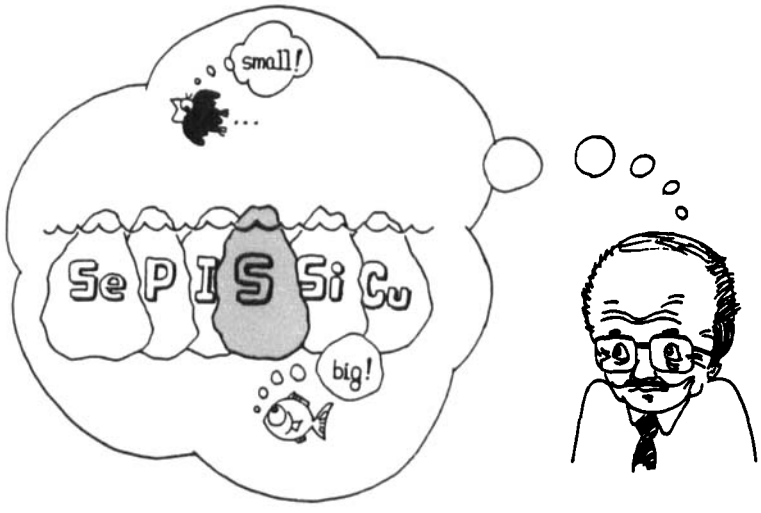
A. INTRODUCTION

When F. K. Beilstein, a Russian chemist, compiled Handbuch der Organischen Chemie into two volumes in 1880-1883, he probably did not realize what would happen in the next one hundred years. How many volumes of Beilstein are available now? We know that more than 30 volumes have been published by now and the number is increasing every decade. Just recently, the number of organic compounds surpassed ten millions. Carbon atom can assume only the valency of four. Yet, organic chemistry, which is centered on carbon atom, has been and is expanding enormously. What would happen in the next few decades? Nobody would dare to make any prediction right now.

What would happen to sulfur chemistry? When one considers how many valencies sulfur atom can assume, probably from zero to six, seven or eight, one can easily say that in the next one hundred years, we will have sulfur centered compounds at least six, seven or eight times of more than those of carbon compounds. Therefore, if we compile Beilstein-type handbook on sulfur molecules, 6 to 7 times more volumes would be insufficient for describing sulfur-centered molecules. What we know now is a very tiny portion of the ostensible surface of the huge iceberg and even that tiny portion would be one of the very very tiny portion of which we can see from our direction, not to mention about the other heteroatoms, as one see the following cartoon. Instead of counting the volume numbers of the handbooks, we would be counting the number of computer discs, in which all the necessary data of sulfur-centered molecules will be found.



One side only
mainly hidden under water !

When I first published with C. C. Price physical organic chemistry of organic sulfur compounds, "Sulfur Bonding", in 1962, the amount of references I refered was only 421 and it took me only two months of 1957. That was enough to cover the story of what I could considered to belong to fit in physical organic chemistry of organic sulfur compounds. In 1969, I wrote another, "Chemistry of Organic Sulfur Compounds" which was translated into Russian and still is used now. It had references of 1555 and took me six months in 1968 to compile. During that decade, many more people started working on this area. In 1976, I edited "Organic Chemistry of Sulfur" which have approximately 2,300 references and this internationally cooperated book took nearly five years to complete. We now see the steady increase, but we are hitting the plateau slowly now. Meanwhile, what one considered to be a small branch is getting to grow. A good example would be "Sulfilimines and Related Derivatives", published by Naomichi Furukawa and myself in 1983. The number of references is 952 and it took us exactly one year.

I mentioned that we are approaching nearly close to the plateau when we try to sort out only those related to physical organic chemistry. Indeed, it was found to be the case. When I finished writing a new book, "Organic Sulfur Chemistry" in 1989 and will be published

soon from the U. S., the number of references was ca. 2,300 but it took me nearly six years to sort out necessary, mainly new data to put in. This may mean that necessary information from my side of physical organic chemistry has got to a steady state. Then one might ask how much I now know in connection with sulfur chemistry. I now feel that I know very little of organic sulfur chemistry at most, if not totally none, after nearly fifty years of research more or less connected with organosulfur chemistry, and I might have contributed a few important findings or concepts in nearly all fields. Thus, all what I can say now is that Sulfur Chemistry has just started and will be developed tremendously in the future if we tackle it from many directions by many earnest workers. The area is so wide and what we do not know now is beyond our imaginations.

Therefore, I will mention only a few unsolved problems which I would hope to be clarified in the next few decades. Much of unsolved problems of chemical behavior of S-atom centered compounds have been touched earlier.[1] Hence, those which were covered earlier would be dealt only briefly and a few additional items will be described here.

B. CHEMICAL BEHAVIOR OF ELEMENTAL SULFUR AND POLYSULFIDES

Vulcanization of rubber with elemental sulfur has been used for one hundred and fifty years and is a very important process. However, the mechanism of rubber vulcanization with elemental sulfur is still not fully understood.[2,3]

Elemental sulfur can assume various forms of allotropes. Some homocyclic neutral rings have been prepared in pure, crystalline states, e.g., S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{13}, S_{18}, and S_{20}.[4] While S_1, S_2, S_3, S_4, and S_5 are known but have not been well characterized, though they would be quite reactive; polymeric sulfur, S_x, can be prepared by melting and quenching the molten sulfur as cold as -20°C. It can be obtained as a rubber-like polymer mixture, which is considered to be a solid solution of a brittle polymer, having a glass melting point of 75°C, in super-cooled liquid S_8. The number of S atom in S_x, is believed to be in the order of 10^5.[5]

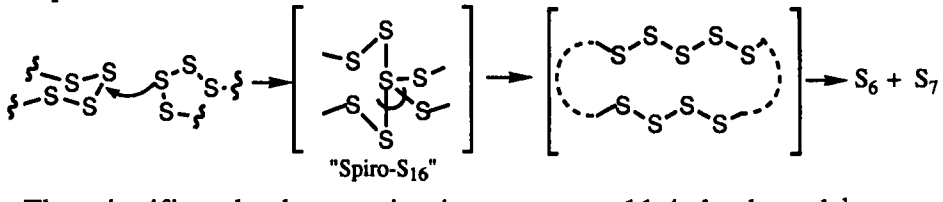
While reactions conceivable to involve S_1, S_2, and S_3 have been

presented in many cases,[6-10] a few interesting but unsolved problems will be presented below.

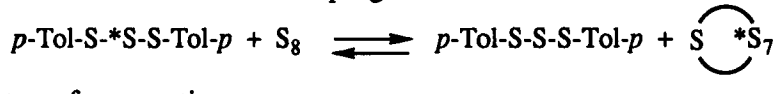
The occurrence of the following amazingly facile disproportionation of S_8 by dissolving the ordinary S_8 in common solvents such as methanol and acetonitrile is interesting,[11] though the equilibrium concentration of S_6 and S_7 was rather low, ca. 1%. This process does not

$$S_8 \rightleftharpoons S_6 + S_7$$

seem to require much energy, probably around or even less than 10 kcal mol^{-1}. Steudel suggested the incipient formation of "spiro-S_{16}" species.[12] Since a certain hypervalent interaction between sulfur atoms in the sulfane rings is expected to operate, there is a possibility that the following mechanistic path, involving ligand coupling within the "spiro-S_{16}" species, a kind of hypervalent species,[13] further expansion of the ring and the final collapse may result in the formation of S_6 and S_7 allotropes.

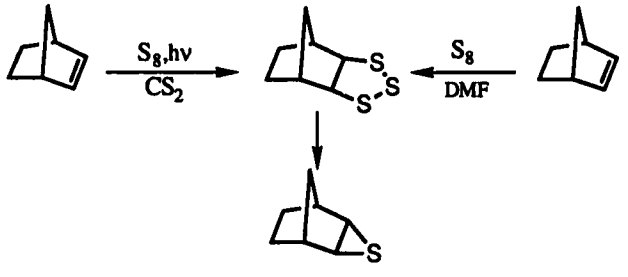


The significantly low activation energy, 11.4 kcal mol^{-1}, required for the sulfur exchange reaction between di-*p*-tolyl trisulfide and elemental sulfur[14] is in keeping with the mechanism.

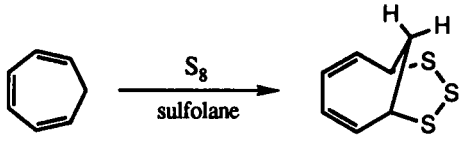


"S_3" transfer reactions

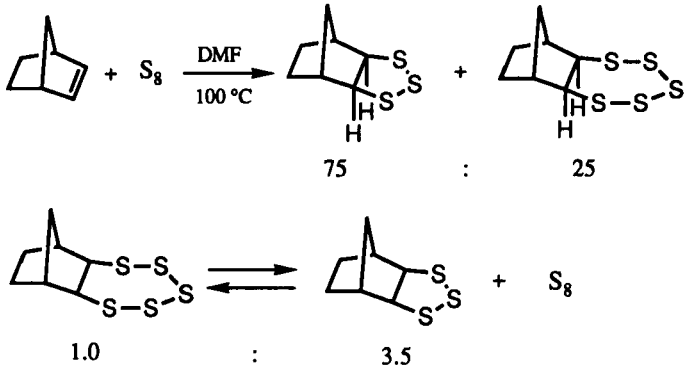
One interesting reaction is the following addition of sulfur to a strained olefin.[15,16]



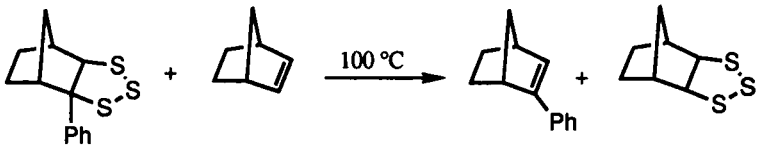
A similar addition of S_3 species was observed in the following reaction.[17]



Recently, a detailed study on the addition of S_3 species to norbornene and the related sulfur transfer reaction has been carried out by Ghosh under the supervision of Professor P. D. Bartlett.[18] In this reaction, not only the trisulfide but also the pentasulfide were obtained as shown below. The pentasulfide seems to be in an equilibrium with the trisulfide.

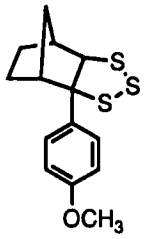


Ghosh made a remarkable observation.[18] Namely, the unit of three S atoms was transferred intermolecularly to other norbornene, e.g., as shown in the following reaction. Apparently, the rate of S_3 transfer in the following reaction is little affected by the change of polarity of the

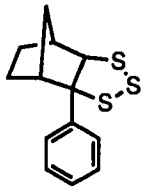


solvent used. There was no change in the rate with solvent from benzene to nitrobenzene, while even the powerful electron-releasing *p*-anisyl derivative, which is known to accelerate the rate of hydrolysis by

a factor of 1,000 compared to that obtained for 1-phenyl-2-norbornyl chloride,[19] was found to react with norbornene less than four times faster than the unsubstituted phenyl derivative. This is unusually slow for any ionic reaction.



Rel. rate 3.5



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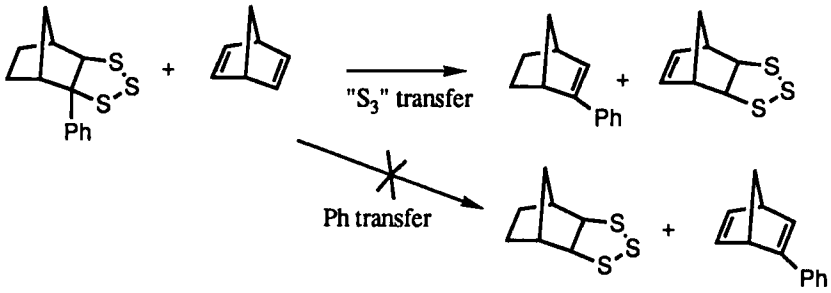
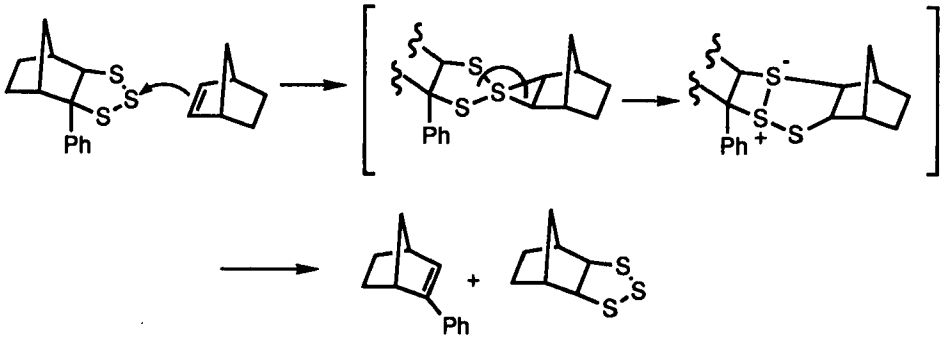
The following experiment has ruled out the possibility of phenyl migration. Though many speculation can be offered for the mechanism

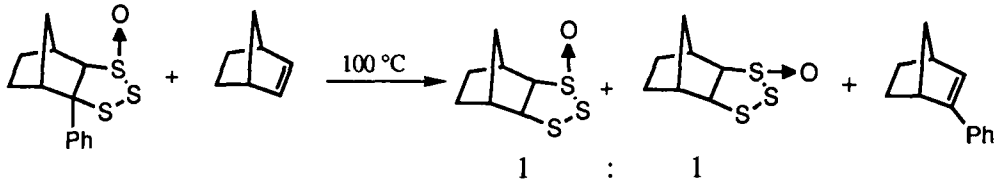


of S_3 transfer from the 2-phenylnorbornene derivative to other norbornene, one possibility may be the following ligand coupling process through the spiro sulfurane shown below.



Even the monosulfoxide was shown to transfer the sulfidic unit to

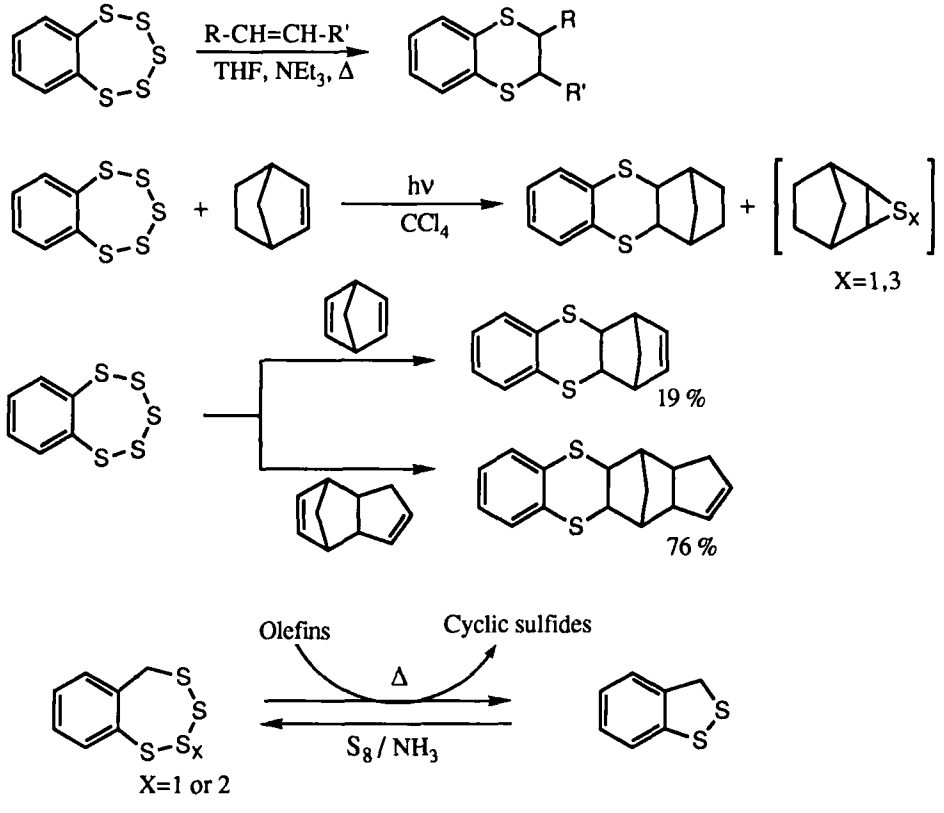
norbornene, though the yield was not quantitative(only roughly 50 %).



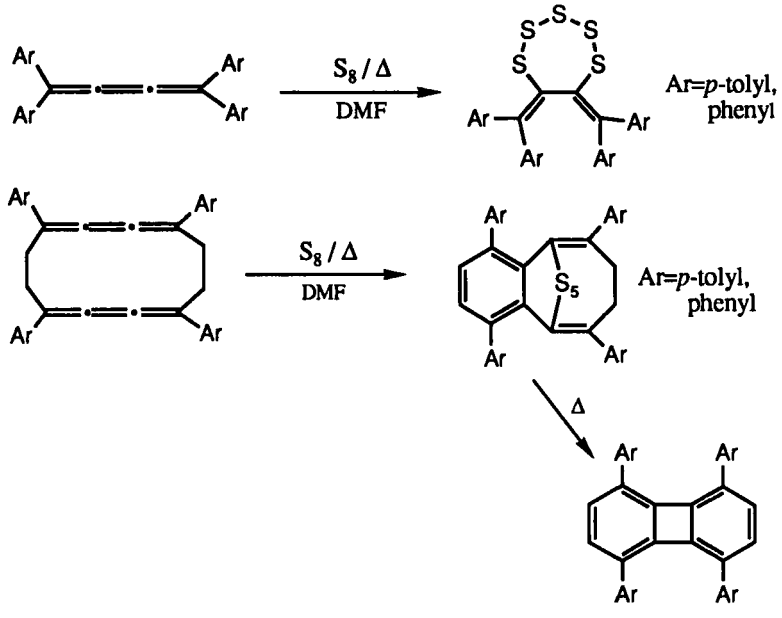
1 : 1

All these "S_3" transfer reactions have never been noticed in the past; however, similar S_x transfer processes, shown above, could be taking place actually in rubber vulcanization and other reactions involving sulfur.

The following works of Sato et al. are also interesting examples.[20]



The following works of Ando et al. are also interesting.[21]

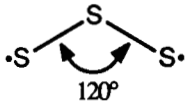


In the pyrolyses of both the norbornane trisulfide and the pentasulfide, two sulfur atoms are extruded from the molecules to afford the episulfide, and the trisulfide, respectively. Some attempts have been carried out to trap the S_2 allotrope but these have failed. The S_2 allotrope could not be the singlet state species as found by Haarp and co-workers,[22] and Schmidt and Görl,[23] who demonstrated that the singlet state S_2 species would undergo the Diels-Alder type addition to conjugate dienes. The allotrope S_2, generated by elemental sulfur around 800 °C and trapped on a cold finger, cooled by liquid nitrogen, is believed to be a biradical and found to react with cyclohexene rapidly even under supercooling, generating only H_2S and benzene.[24] Therefore, the extrusion of the S_2 unit from the trisulfide and the pentasulfide may not be a simple generation of S_2 allotrope of either singlet or triplet state. Obviously, some other unknown processes, similar to that suggested by Huisgen,[25] would be operating.

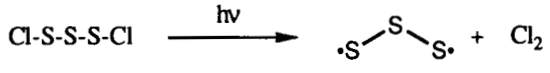
Since the biradical S_2 allotrope can be readily obtained in crystalline form, while only ca. 13 kcal mol^{-1} is necessary to convert

triplet state S_2 to the singlet S_2, one may develop an interesting chemistry using prepared pure S_2 allotrope.

The S_3 allotrope of the ground state is also believed to be a biradical species and has the following structure.[7]

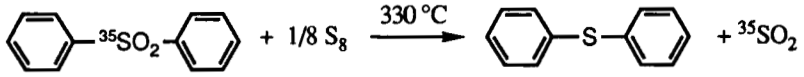


This was prepared in benzene solution by the following reaction and has a deep red color.

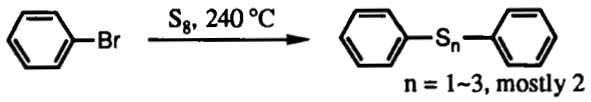


When elemental sulfur is heated above 250 °C, a deep red color develops. This deep red color is believed to be due to the formation of triplet S_3 species, though the equilibrium concentration of S_3 species would be less than 1 %.[7]

Diphenyl sulfone is a very stable compound and can be distilled at 379 °C without decomposition under normal atmospheric pressure. However, when diphenyl sulfone is heated in red molten sulfur at above 300 °C, the following reaction readily takes place.[26] By the use of ^{35}S-labelled diphenyl sulfone, the resulting diphenyl sulfide was found to have lost ^{35}S label.



Bromobenzene was found to react with elemental sulfur even at a considerably lower temperature, i. e., 250 °C, affording quantitatively diphenyl polysulfide, as shown below.[27]



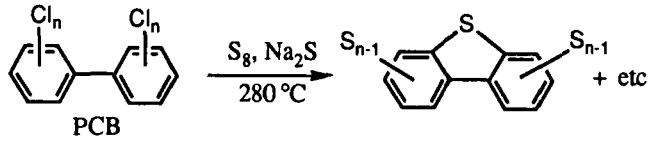
Competitive experiments of substituted bromobenzenes with

elemental sulfur have been carried out and the effect of polar substituents has been found to be very small.[28] This is also in accordance with the homolytic nature of the aromatic substitution and the deep red color always developed during the reaction.

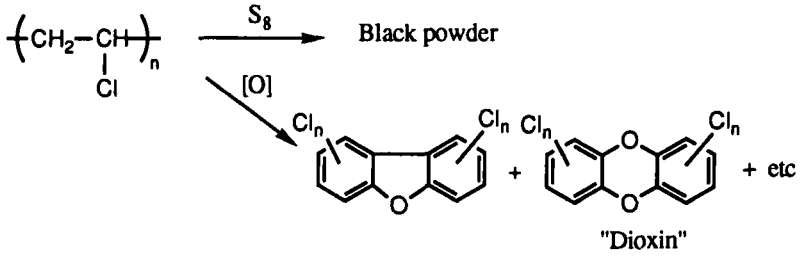
When *ipso*-^{14}C substituted diphenyl sulfone was used for the reaction with elemental sulfur, the resulting diphenyl sulfide was found to retain ^{14}C at the *ipso*-position of resulted diphenyl sulfide.[29] Thus, the reaction has been suggested to be a homolytic substitution, presumably involving the red colored S_3 biradical.

The reactivity of this S_3 biradical species may be tested by treating diphenyl sulfone or bromobenzene with the freshly prepared S_3 allotrope in benzene solution.

One good outcome of this finding is the successful dechlorination of toxic polychlorinated aromatic hydrocarbons, such as polychlorinated diphenyls, commonly known as PCB, which have deprived many many lives all over the world. Upon simple heating of PCB with red-colored hot liquid sulfur above 280 °C, practically all the chlorine atoms are eliminated, nearly to the extent of less than 10 ppb, and resplaced mostly by sulfur; thus PCB is completely detoxicated.[30,31]



Polyvinyl chloride, PVC, is perhaps one of the most useful plastics and used for water pipes, floorings, green house covering and many others. However, once their useful functions are over, the waste disposal of the old PVC becomes a serious problem, since inceneration of PVC is known to give very toxic compounds, such as polychlorinated dibenzofuran and polychlorinated dibenzodioxane, commonly called as dioxin, which are considered to be more than a thousand times toxic than PCB.[31] Therefore, it is dangerous to put PVC into an kiln for burning household wastes. Here again, by heating waste PVC with elemental sulfur at around 250 °C, one can eliminate chlorine nearly completely after a few hours and obtain a black powdery material which contained sulfur.

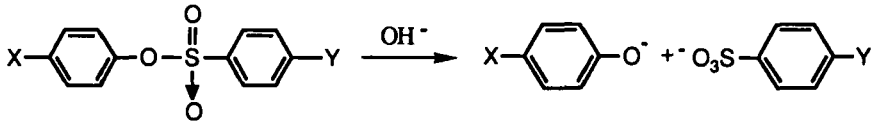


This can be burned in an ordinary kiln or used as a heat-absorbing material for flower and vegetable beds. Addition of sodium sulfide into the reaction mixture of elemental sulfur and either PCB or PVC gives an excellent result in eliminating chlorine from the polychlorinated hydrocarbons. Since the process is very simple while the cost of operation is so cheap, heating with elemental sulfur would be quite useful for dechlorinating detoxication of PCB and other polychlorinated hydrocarbons, which are now regarded as one big source of toxic public hazards. Once these polychlorinated compounds are converted to dechlorinated, sulfur-containing compounds, they are no longer so toxic as the original polychlorinated materials, since mammalians have enzymatic systems such as FAD-containing monooxygenase to oxidize water-insoluble divalent sulfur compounds to water-soluble oxides.

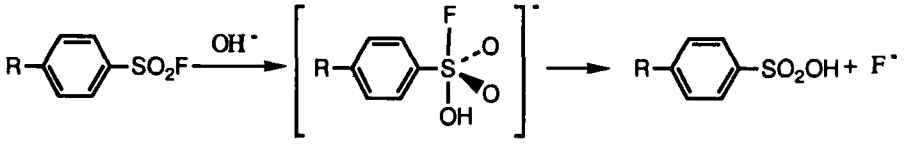
C. NUCLEOPHILIC SUBSTITUTIONS ON THE SULFUR ATOM-POSSIBLE INVOLVEMENT OF A σ-SULFURANE

Many works have been carried out to elucidate the mechanisms of hydrolyses of aryl arenesulfonates using ^{18}O tracer and others.[30-35]

All the ^{18}O tracer experiments and stereochemical results do not seem to favor the incipient formation of any hypervalent intermediate., There are many kinetic experiments which indicate marked rate enhancements by polar substituents in the hydrolyses of substituted benzenesulfonyl halides[36,37] and phenyl esters.[38] In the last example, shown below, ρ_x and ρ_y were found to be 3.0 and 2.4, respectively.[38]



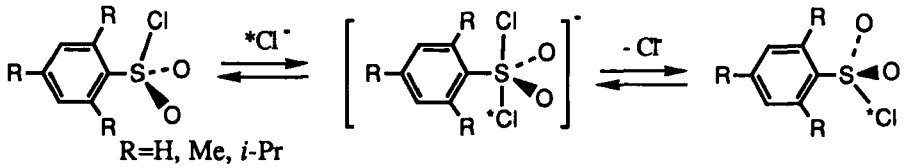
Another example done by Ciuffarin et al.,[39] is shown below. In this reaction, the Hammett ρ-value was also found to be quite large, i. e., ρ=2.8. This large ρ-value is in accordance with the similarly large



ρ-value observed in nucleophilic substitution on Si, which is believed to proceed through formation of the five-coordinate Si intermediate, which has a trigonal bipyramid structure.[40] A recent criticism of this interpretation of ρ-values[39] may not be valid, because of the possible involvement of a "sulfene" type intermediate in the aminolysis of arenemethylsulfonyl halides.

Usually one does not observe a noticeable α-effect in nucleophilic substitution on the sp^3 carbon atom.[40,41] However, in the nucleophilic substitution on the sp^2 carbon, which involves the initial formation of an addition intermediate, and also in the nucleophilic addition on the *sp* carbon atom, markedly large α-effects are observed.[40,42] Kice et al. earlier observed a marked α-effect in the nucleophilic substitution on the sulfonyl sulfur atom with hydroperoxide ion.[43] A markedly large α-effect was also observed by us in the nucleophilic substitution of *p*-toluenesulfonyl chloride with hydrazine.[44] These markedly large α-effects may also suggest the involvement of an initial addition intermediate in the nucleophilic substitution on the sulfonyl sulfur atom.

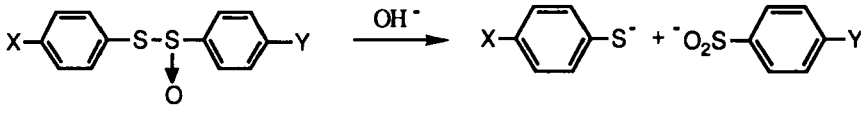
There is an interesting observation that *o,p*-substitutedsulfonyl chlorides undergo the Finkelstein reaction with radioactive Cl^- ion, as shown below, where the bulky substituent accelerates the rate of the reaction several fold.[45]



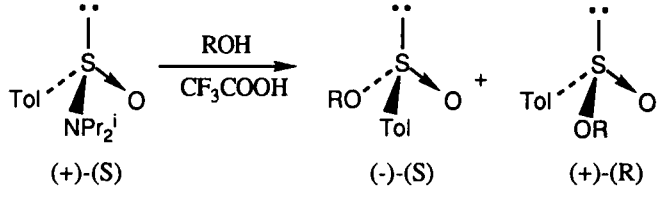
R=H, Me, *i*-Pr

Mikołajcyk et al.[45] suggested that the initial sulfonyl chloride, which has a sp^3 like tetrahedral structure, would be sterically strained and the steric strain would be reduced by forming the hypervalent intermediate of trigonal bipyramid structure.

By the use of the ^{18}O-labelled thiolsulfinates, the alkaline hydrolysis of thiolsulfinate was shown to take place by the initial nucleophilic attack of the OH^- ion on the sulfinyl sulfur atom.[46] The effect of polar substituents was observed by kinetic experiments on the following reaction.[47] Here again, markedly large values of ρ_x (2.4) and ρ_y (1.6) were obtained.[47]

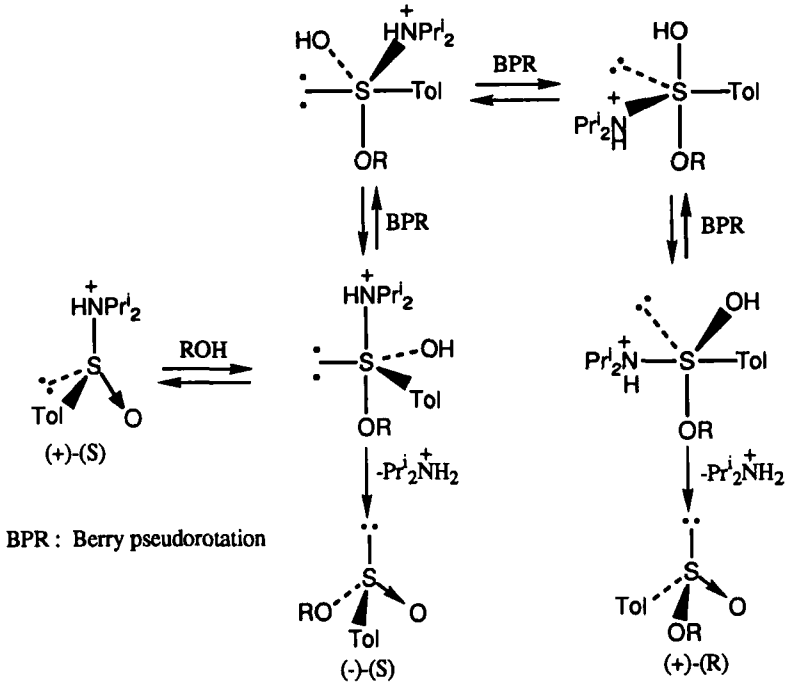


The most striking observation would be that the acid catalyzed alcoholysis of optically active (+)-*N*,*N*-diisopropyl toluenesulfinamide gave both the inverted and the retained sulfinyl esters.[48] Mikołajcyk[48] believes that the acid catalyzed alcoholysis proceeds via formation of



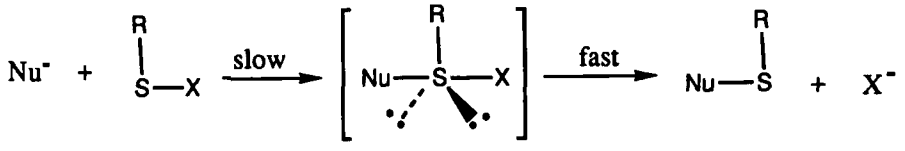
(+)-(S) (-)-(S) (+)-(R)

the σ-sulfurane, which undergoes Berry pseudorotation to afford the sulfinyl ester of retained configuration or the straightforward inverted ester. When methyl alcohol was used, the amount of retention was found to be 31 %, while in alcoholysis with c-Hex-OH the amount of retention was 74 %. Apparently the bulkiness of both attacking alcohol and leaving dialkylamino group exert an important effect on the steric course of the reaction. Thus, he has postulated the following mechanism.



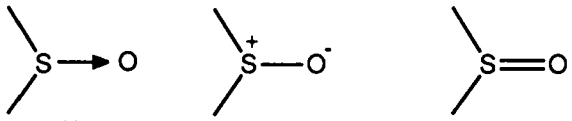
Although the ease of pseudorotation has to be examined more widely with various other examples, this stereochemical experiment, along with our findings on ligand coupling reactions within σ-sulfuranes, described later, seem to indicate rather clearly that nucleophilic attack on the sulfinyl sulfur atom involves the formation of a hypervalent intermediate, i. e., σ-sulfurane. This means that the reaction is a ligand exchange within σ-sulfurane and not a S_N2 process.

The nucleophilc substitution on the sulfenyl sulfur atom has remained to be the most intriguing problem. However, many accumulated works,[49-54] seem to support the importance of the nucleophilic attack on the central sulfur atom. Thus, most of the available data seems to favor the incipient formation of a σ-sulfurane intermediate, even in the nucleophilc substitution on the sulfenyl sulfur atom as shown below.



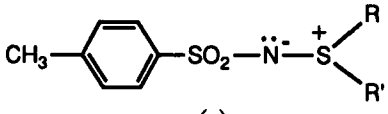
D. EXPRESSION OF THE SEMIPOLAR OR DOUBLE BOND CHARACTER OF S-O, S-N, AND S-C BONDS IN SULFOXIDES, SULFILIMINES AND SULFONIUM YLIDES

When the book "Sulfur Bonding" was first written in 1962,[55] the S-O bonds in sulfoxides were described as semipolar, since the bond force constants are small, ca. 6-8x10^5 dyne cm^{-1}, similar to that of the N-O bond of pyridine N-oxide despite the rather small bond moment, ca. 2.5 D, measured at the time. The bond moments of diphenyl and some substituted diphenyl sulfoxides were carefully remeasured later and the average bond moment of the sulfoxide linkage was found to be as large as 4.76 D.[56] Sulfoxides are known to have a pyramidal structure and to be intrinsically chiral.[57] The strong hydrogen-bonding property of sulfoxide,[58-60] the small value of the calculated bond order,[61] and the relatively small bond dissociation energy of the S-O linkage in sulfoxides (86 kcal mol^{-1} average) as compared to that in sulfones (112 kcal mol^{-1} average), seem to indicate rather convincingly that the S-O linkage in the sulfoxide is best expressed as a semipolar single bond (a) or (a') rather than a covalent double bond (b). This does not mean that

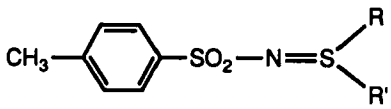


(a) (a') (b)

"back-donating bonding" involving *p* orbitals on oxygen and 3*d* orbitals of the sulfur atom is not important. However, the "back-donating bond" cannot be an ordinary π-bond between *p* orbitals of the olefinic double bond or of ketones. So many people express sulfinyl linkage as a covalent double bond. Should we leave such an expression of the sulfinyl linkage as a covalent double bond without any warrant? The nature of the S-N linkage in sulfilimines, in such a compound as *N-p*-toluene sulfonylsulfilimines, was once suggested to have the ylene structure (d) rather than the ylide structure (c).[62] However, the longer S-N linkage of the sulfilimine, the rather small bond force constant of the S-N bond (ca. 4.4x10^5 dyne cm^{-1}) calculated from the stretching vibration of the S-N bond around 930-950 cm^{-1}, the pyramidal



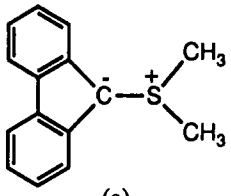
(c)



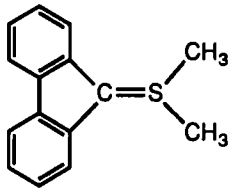
(d)

structure of the sulfilimine, the dipole moment measurements, the MO calculation, and the photo-electron spectra all seem to support a semipolar pyramidal structure for the sulfilimine.[63,64]

In the case of the sulfonium ylides, one seldom sees the ylene structure. Indeed, the stable ylide synthesized by Wittig et al., shown below, was found to have a large dipole moment, 6.20 D, clearly showing that the molecule is better represented by the ylide structure (e) rather than the ylene structure (f).[55] From the value of the shortest



(e)

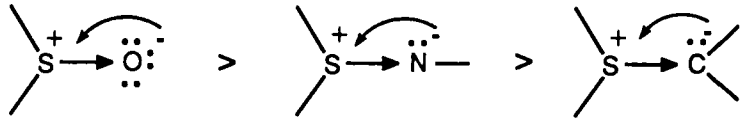


(f)

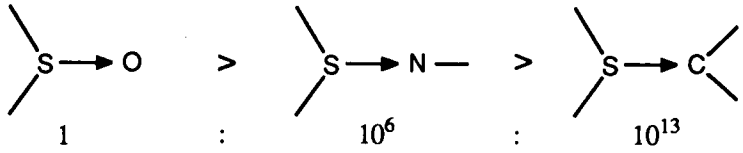
linkage of C-S of the sulfonium ylide, 1.707 Å, one can calculate its bond force constant to be 3.26×10^5 dyne cm^{-1}.[63] This is even smaller than the average value of the *N*-*p*-tosylsulfilimines, i. e., 5.42×10^5 dyne cm^{-1}, which is smaller than that of the S-O linkage of the sulfoxide, i. e., ca. 7.0×10^5 dyne cm^{-1}. Probably, " back-donating bonding" will be greatest in the S-O linkage of the sulfoxide and weakest in the S-C bond of the sulfonium ylide. Even in the strongest S-O linkage of the sulfoxide, the "back-donating bond" would be nowhere near the normal π-bond, expressed by a legitimate double bond.

All these differences of bond force constants and the extents of "back donation" seem to reflect on the relative rates of pyramidal inversion, as shown below.[64]

Back Donation:

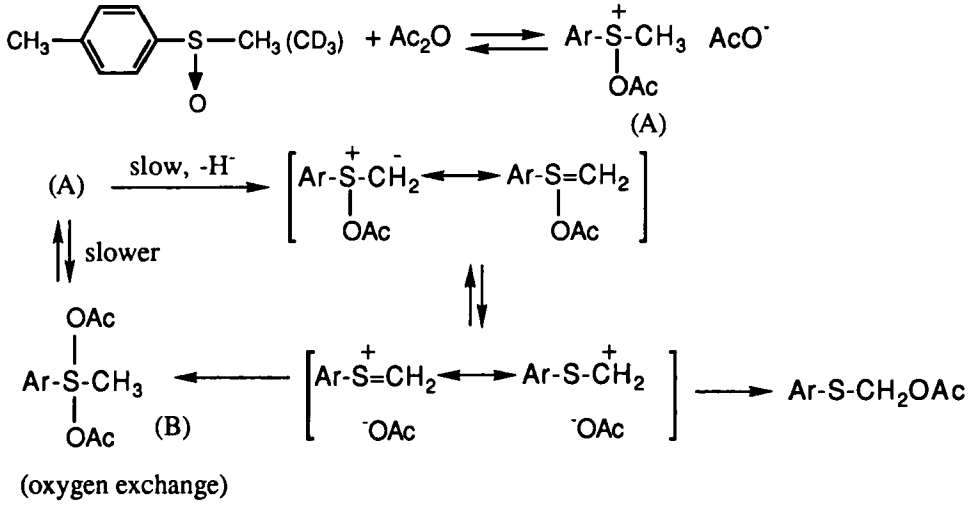


Relative rates of Pyramidal Inversion:



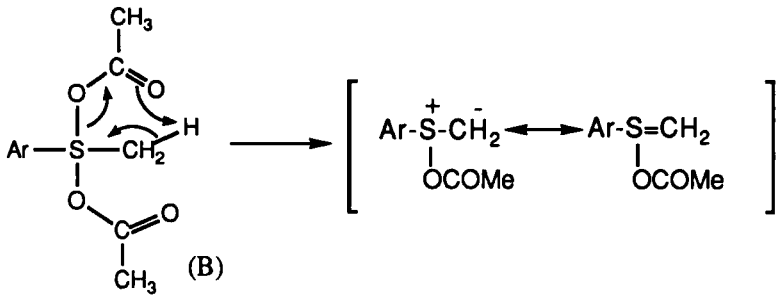
E. DOES THE PUMMERER REACTION INVOLVE σ-SULFURANE?

The Pummerer reaction of substituted phenyl methyl sulfoxide with acetic anhydride has been shown to proceed by the following mechanistic scheme,[65,66] since the seleno-analog of σ-sulfurane was isolated in the similar reaction of a selenide with benzoyl peroxide.[67,68] When X is nitro in the following reaction, the isotope effect, k_H/k_D, is only 3.0.



Thus, it was once suggested that a sulfurane-type intermediate (B) may also be formed in the Pummerer reaction. Proton removal takes place through a six-membered cyclic transition state, shown below, with

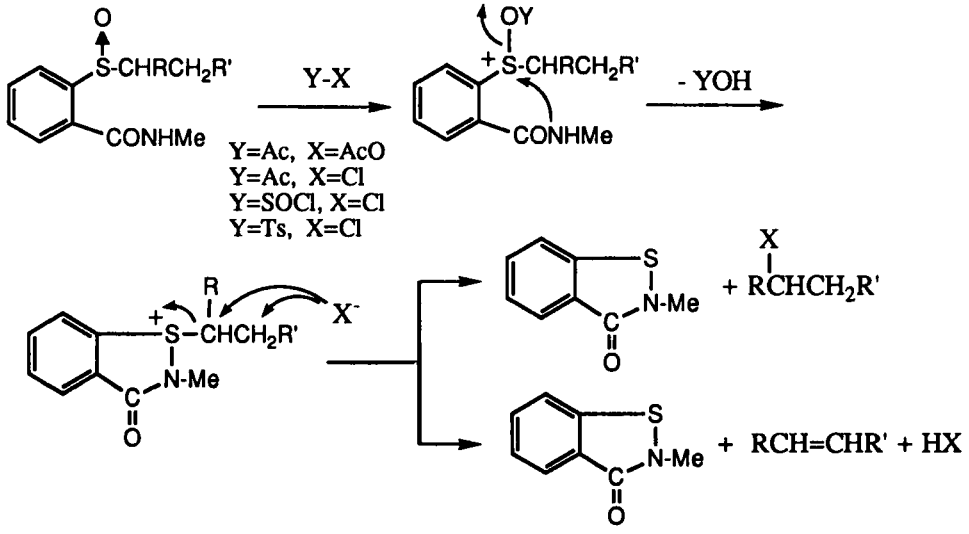
an angle close to 110-120°, as in the *Ei* reaction, via either a five- or six-membered cyclic transition state with isotope effects generally in the range of 3-4.[69] The much slower rate of oxygen exchange than that of the rearrangement in the Pummerer reaction, however, can alone rule out the scheme involving the sulfurane (B).



(B)

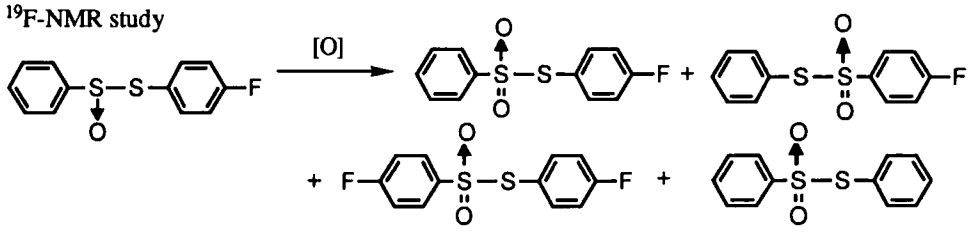
The acid-catalyzed Pummerer reaction of *o*-(*N*-methylcarbamoyl)-phenyl sulfoxide with acetic anhydride and those with various acyl halides were found to be rather unusual.[65-70] However, even in this reaction there was no indication of the intermediary formation of any σ-sulfurane.[70] Thus the following mechanistic scheme has been suggested.[70]

Is there not any example of the Pummerer reaction which proceeds via formation of the σ-sulfurane?

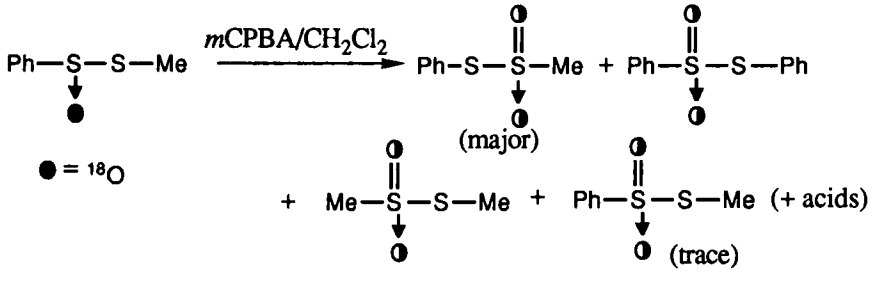


F. WHY ARE "α-DISULFOXIDES", "α-KETO SULFOXIDES", AND "α-SULFINYL NITRITES" SO UNSTABLE?

Earlier, "α-disulfoxide" was considered to be formed in the process of biochemical oxidation of cystine.[71] However, the IR spectrum and the authentic synthesis has proved that it was indeed the corresponding thiolsulfonate. Modena and co-workers[62,72] suggested the formation of "α-disulfoxide" as an incipient intermediate in their kinetic studies on the electrophilc oxidation of the disulfide and the thiolsulfinate. However, "α-disulfoxide" would be so unstable that it would immediately isomerize to the corresponding thiolsulfonate. Barnard[73] also tried to prepare the α-disulfoxide and failed. Kice and co-workers[74] attempted to detect the α-disulfoxide by looking at ^{19}F-NMR in the following electrophilc oxidation at 120 °C. They failed to detect any intermediary α-disulfoxide and then suggested that the S-S bond energy of the α-disulfoxide would be less than 20 kcal mol^{-1}.



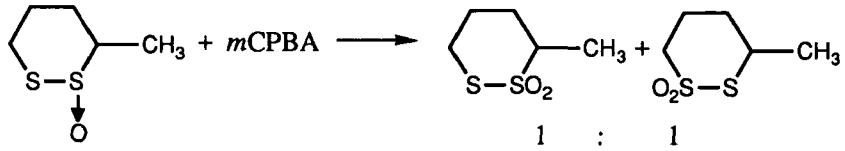
When *S*-methyl benzenethiolsulfinate was oxidized with an electrophilic oxidant such as *m*CPBA, more than 30 % of *S*-phenyl methanethiolsulfonate was found to be formed along with other compounds as shown below.[75-77]



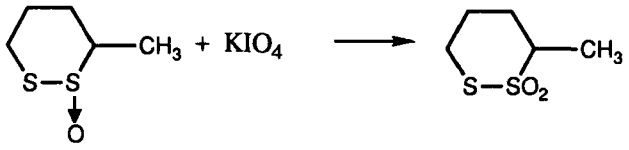
By the use of ^{18}O-labelled S-methyl benzenethiolsulfinate, the maigration of ^{18}O was found to be nearly completely intramolecular.[77] The intramolecular nature of ^{18}O migration clearly seems to reveal the initial formation of the α-disulfoxide.

Another interesting example would be the formation of the two isomers of dithiane-dioxide in the electrophilc oxidation of dithiane monooxide with *m*CPBA, while the nucleophilic oxidation of the same compound gave the only one isomer, as shown below.[78,79]

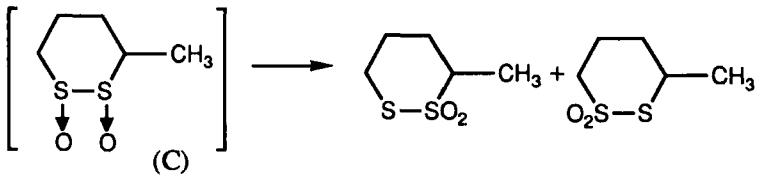
(Electrophilc Oxidation)



(Nucleophilic Oxidation)



In the former reaction, it is considered that only the divalent sulfur atom is attacked by *m*CPBA, a typical electrophilic oxidant, to incipiently form the α-disulfoxide (C), which eventually rearranges to afford the two isomeric products of the cyclic thiolsulfonate.[62,72-76,78]

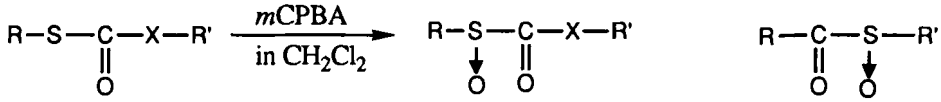


Meanwhile. Freeman and co-workers[79,80] have carried out the electrophilic oxidation of *S*-*t*-butylthiolsulfinate with *m*CPBA at around -45 °C and obtained NMR spectra which can only be ascribed to the α-disulfoxide. However, it was not possible to isolate the corresponding α-disulfoxide.

Thus, the formation of the α-disulfoxide(C) as the initial intermediate in the electrophilc oxidation of the thiolsulfinate seems to be

beyond any doubt. However, why is the α-disulfoxide so unstable? The α-disulfone is quite stable and even the sulfinyl sulfone can be isolated, though it is somewhat less stable than the disulfone.

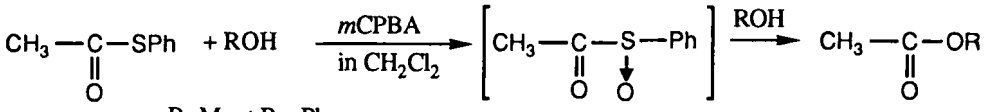
Although treatment of mono- and dithiocarbonates and monothiocarbamates with *m*CPBA readily afforded the corresponding sulfoxides, as shown below,[81,82] many attempts to prepare the



X = O, S, NR'
R=CH_2Ph, Et, *i*-Pr, etc.
R'=CH_3, cyclo-Hex, *n*-Pr, Et, *iso*-Bu, etc.

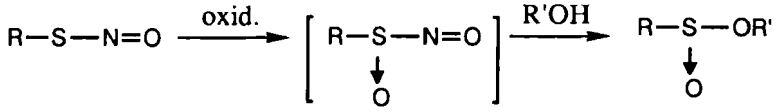
(D)

"α-keto sulfoxide" (D) have been unsuccessful,[83] though it was assumed to be the intermediate in the following reaction.[84]

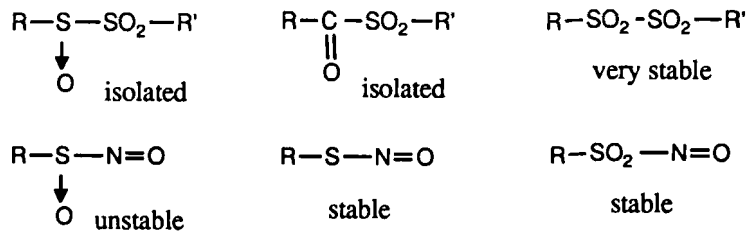


R=Me, *t*-Bu, Ph

The thionitrite, R-S-N=O, and the sulfonyl nitrite, R-SO_2-N=O, are both relatively stable and isolated, but the sulfinyl nitrite, R-SO-N=O, has never been isolated, but would be the unstable intermediate in the oxidation of thiols with N_2O_5.[85,86]



Is there any reason why these sulfinyl compounds are so unstable? Both the *S*-unoxidized and *S*-dioxidized species are isolated in stable forms, as shown below.



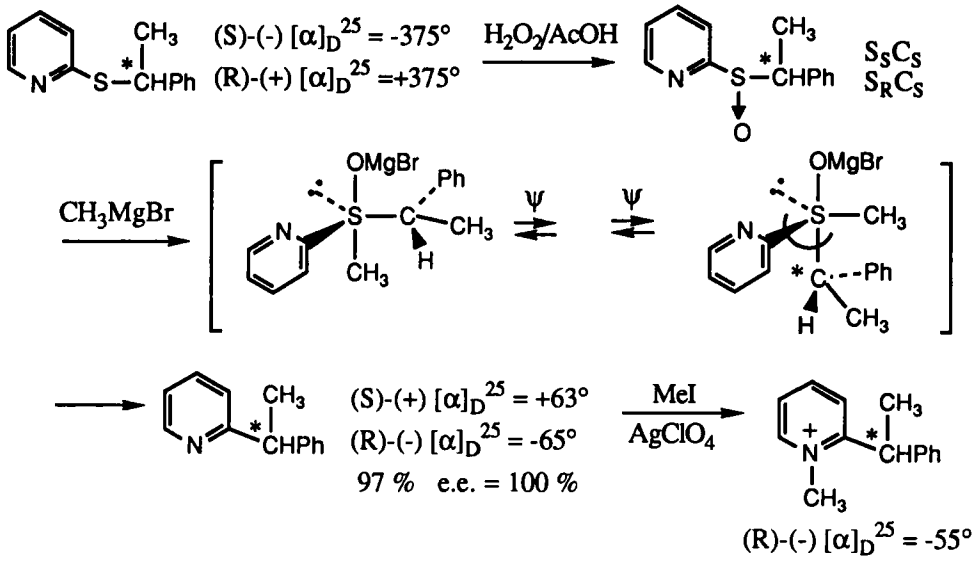
G. RELATIVE EASES OF LIGAND EXCHANGE, LIGAND COUPLING AND PSEUDOROTATION WITHIN α-SULFURANES

Numerou examples of relatively stable σ-sulfuranes have been isolated[87-89] and the markedly strong hypervalent type interactions have been observed,[90] even between the sulfenyl sulfur atom and relatively weakly nucleophilic heteroatoms.[91] However, no stable σ-sulfurane bearing carbon-centered ligands at axial coordinates have been isolated, though what appeared to be the formation of σ-sulfurane bearing tetra(pentafluorophenyl) groups on the sulfur atom was noticed earlier from ^{19}F-NMR neasurements by Sheppard.[92] All the stable σ-sulfuranes which have hitherto been isolated have electro-negative heteroatom-centered ligands at the axial positions, while the rates of pseudorotation have also been measured with those σ-sulfuranes bearing heteroatom-centered ligands.[93-95]

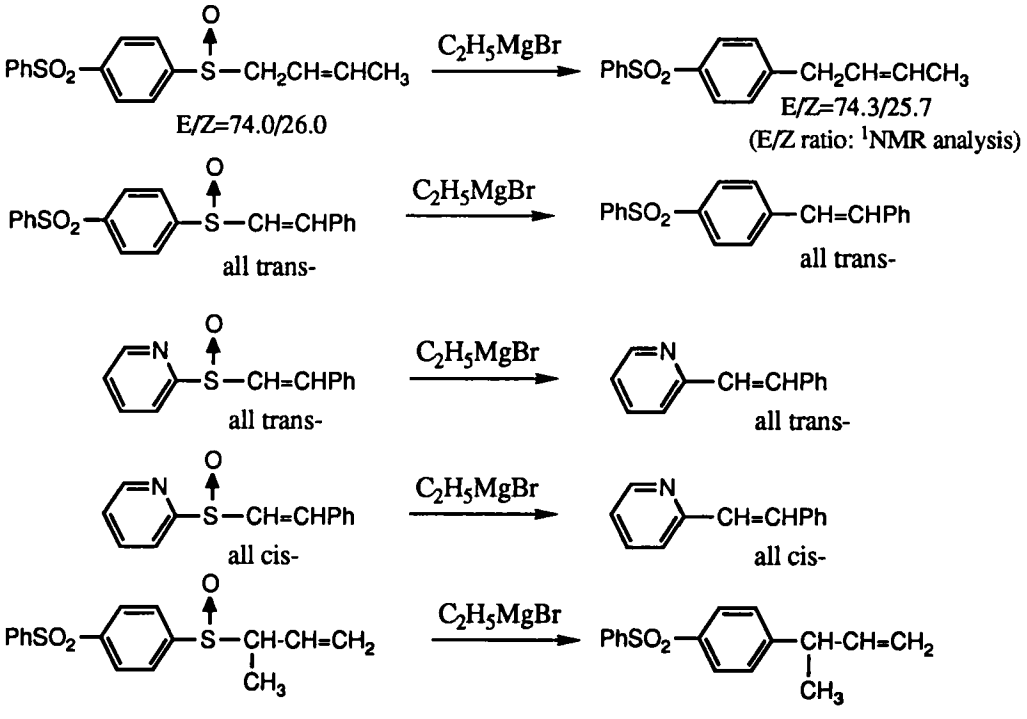
The initial formation of the σ-sulfurane has been assumed in the ligand exchange reactions on both sulfinyl and sulfonyl sulfur atoms.[96] However, here again, no kinetic measurement has been successfully carried out when the entering and/or leaving group is the carbon-centered ligand. Thus, the relative eases of ligand exchange and pseudorotation of carbon-centered ligands on the hypervalent sulfur atom are by no means known.

Another interesting reaction which would involve the initial formation of the σ-sulfurane is the ligand coupling reactions, which we have postulated.[13]

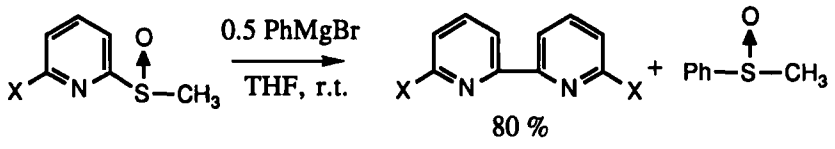
Numerous reactions involving trivalent sulfur compounds and nucleophiles have been suggested to proceed through ligand coupling within σ-sulfuranes formed as intermediates,[13] since the finding of diaryls in the treatment of triarylsulfonium halides with aryl-lithium.[97,98] There have been numerous examples of ligand coupling within hypervalent phosphoranes.[99] However, it was after the discovery of convincing stereochemical evidence,[100,101] shown below, that the concept of ligand coupling within the hypervalent intermediate was postulated.[98] This concept was extended not only to the reactions of the σ-sulfuranes and phosphoranes, but also of organometallic compounds.[102]



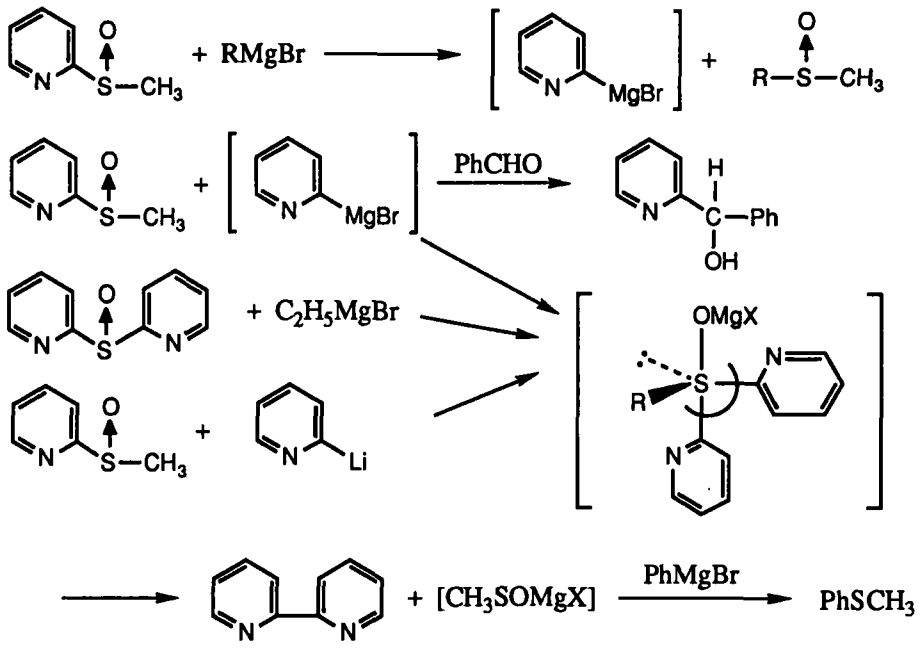
Similar retentions of configuration were observed in the ligand coupling reactions of allylic and vinylic sulfoxides with Grignard reagents, as shown in the following equations.[103]



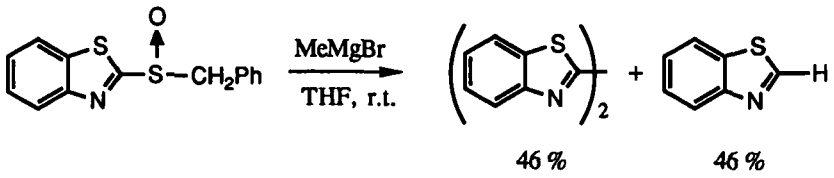
One interesting reactions is the following formation of 2,2'-dipyridyl.[104] This process obviously involves the initial ligand



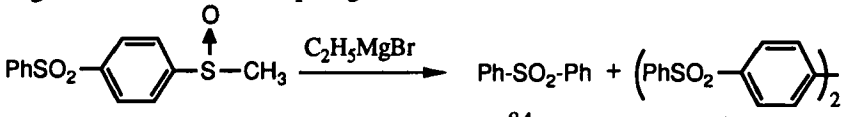
exchange and sunsequent ligand coupling of two 2-pyridyl groups. Indeed, 2-pyridylmagnesium bromide can be trapped in the presence of banzaldehyde, while similar couplings were observed as shwon below.[105a] A similar reaction takes place with the 2-quinolyl derivative.[105b,c]



A similar reaction was observed when 2-benzothiazolyl benzyl sulfoxide was treated with methylmagnesium bromide, as shown below.



One might wonder if the ease of the ligand exchange is associated with the electronegativity of the ligand involved in the reaction, since 2-benzothiazolyl group is substantially more electronegative than 2-pyridyl group, as diagnosed by the ^{13}C-NMR chemical shifts, i. e., 176.9 ppm and 163.6 ppm, respectively. However, the less electronegative benzenesulfonylphenyl group, as diagnosed by the ^{13}C-NMR chemical shift, i. e., 151.9 ppm, was found to preferentially undergo ligand exchange rather than coupling, as shown below.[106]

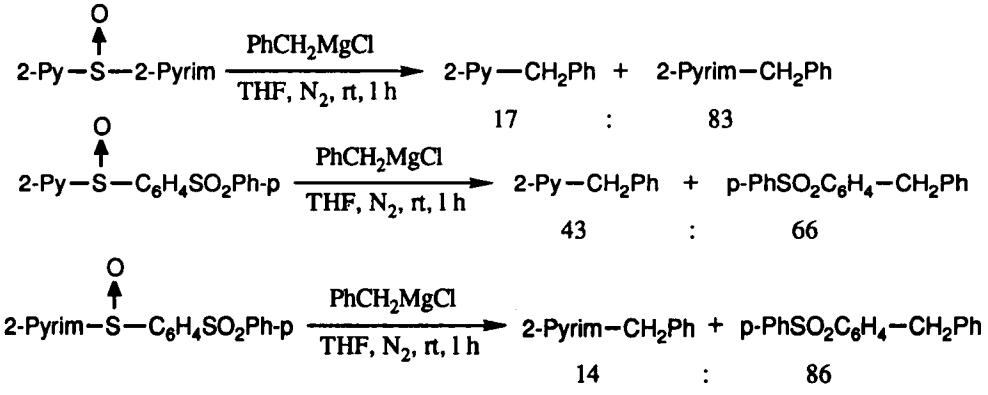


84 : 16

The 2-thienyl group, which is considered to have a similar electron-withdrawing property to the benzenesulfonylphenyl group, as established from the ^{13}C-NMR chemical shift, is another ligand which undergoes predominant ligand exchange, even in the reaction of benzyl 2-thienyl sulfoxide with Grignard reagents.[107]

When one ligand is either the pyridyl or the benzenesulfonylphenyl group in the sulfoxide, the benzylic group was found to couple preferentially over the allylic group, which in turn is a better group to couple with 2-pyridyl or benzenesulfonylphenyl groups than the vinylic group in the reactions of the sulfoxides with Grignard reagents.[103]

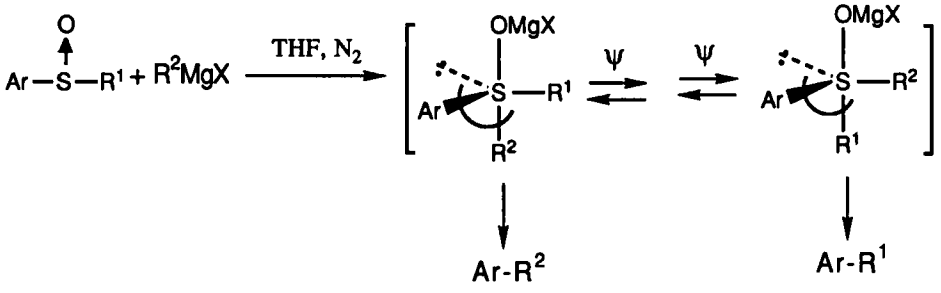
Another set of interesting example is illustrated by the following equations.[102,108]



Now the main questions would be concerned with what are the factors which control the eases of ligand exchange, ligand coupling and topological transformation.

Earlier, it was mentioned that there is no example which deals with any topological transformation such as Berry pseudorotation or turnstile rotation, which involves carbon-centered ligands on the hypervalent atoms.

In the following reactions of benzyl aryl sulfoxides and benzylic Grignard reagents, two products are obtained, presumably both through direct ligand coupling and consecutive pseudorotation and ligand coupling.



Some representative data obtained in the above reaction are listed in Table 1. Inspection of the data reveals clearly that the coupling mode between the *p*-benzenesulfonylphenyl group and the benzylic group is quite different from that between the 2-pyridyl and benzylic groups. In the reaction of benzyl *p*-benzenesulfonylphenyl sulfoxide with *p*-methylbenzylmagnesium chloride and also in that between *p*-methylbenzyl *p*-benzenesulfonylphenyl sulfoxide and benzyl Grignard reagent, the benzyl group tends to couple preferentially with the aryl group. Substitution of an electron-donating methyl group at the *p*-position of the benzyl group clearly reduced the amount of coupling product between the aryl and *p*-methylbenzyl groups. In contrast, the substitution of an electron-withdrawing chloro group at the *p*-position of the benzyl group was found to increase remarkably the amount of coupling product between *p*-chlorobenzyl and the aryl groups. Even in the reaction of *p*-chlorobenzyl 2-pyridyl sulfoxide with benzylmagnesium chloride, the major coupling product was 2-(*p*-chloro-

Table 1. Ratios of coupling products in the above reaction[a]

Entry Ar	R^1	R^2	Rt $ArR^1:ArR^2$ ratio	Total yield(%)	50 °C $ArR^1:ArR^2$ ratio	Total yield(%)
1. 2-Py	p-$CH_3C_6H_4CH_2$	$PhCH_2$	16 : 84	55.3	20 : 80	56.8
	$PhCH_2$	p-$CH_3C_6H_4CH_2$	44 : 56	51.7	52 : 48	48.2
2. p-Bsp	p-$CH_3C_6H_4CH_2$	$PhCH_2$	20 : 80	53.3	19 : 81	47.5
	$PhCH_2$	p-$CH_3C_6H_4CH_2$	77 : 23	49.5	46 : 54	50.5
3. 2-Py	o,p-$(CH_3)_2C_6H_3CH_2$	$PhCH_2$	17 : 83	57.3		
	$PhCH_2$	o,p-$(CH_3)_2C_6H_3CH_2$	41 : 59	44.3		
4. p-Bsp	o,p-$(CH_3)_2C_6H_3CH_2$	$PhCH_2$	12 : 88	59.4		
	$PhCH_2$	o,p-$(CH_3)_2C_6H_3CH_2$	47 : 53	57.8		
5. 2-Py	p-$ClC_6H_4CH_2$	$PhCH_2$	65 : 35	48.3		
	$PhCH_2$	p-$ClC_6H_4CH_2$	9 : 91	47.1		
6. p-Bsp	p-$ClC_6H_4CH_2$	$PhCH_2$	65 : 35	53.8		
	$PhCH_2$	p-$ClC_6H_4CH_2$	6 : 94	50.0		
7. 2-Py	o,p-$Cl_2C_6H_3CH_2$	$PhCH_2$	92 : 8	29.1		

[a] 2-Py=2-pyridyl; p-Bsp=p-benzenesulfonylphenyl

benzyl)pyridine (entry 5 in Table 1). Even more noticeable is the preferential coupling of the o,p-dichlorobenzyl group with the 2-pyridyl group (entry 7 of Table 1).[109]

Unless we assume a topological transformation such as Berry pseudorotation, the preferential coupling of o,p-dichlorobenzyl with 2-pyridyl groups, or other ligand coupling, to form $Ar\text{-}R^1$ type compounds may not be explained.

Here again, however, pseudorotation seems to be accelerated relative to coupling as temperature is raised (entry 1 and 2 of Table 1).

These data clearly show that a slight change of the stereoelectronic effect of S-substituted ligands appears to change the mode of coupling, due to the change of the ease of pseudorotation of the intermediary σ-sulfurane. The facile change of pseudorotation by the slight variation of stereoelectronic environment of the involved ligand was also observed recently by Mikołajcyk[48] in ligand exchange, i. e., the acid-catalyzed

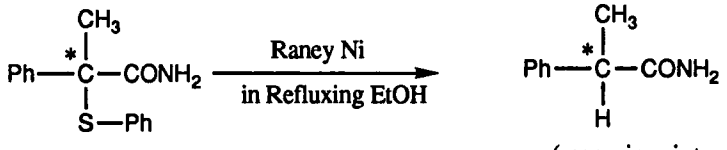
nucleophilic substitution of optically active sulfinyl amides with alcohols, as mentioned previously.

The factors which would control the ease of pseudorotation within the σ-sulfuranes are not known at present.

One factor which appears to be quite legimate is that the central atom in the σ-sulfurane is valence-shell expanded and hence trends to resume the normal and stable octet by extruding a ligand or two with a pair of electrons; this serves as the main driving force for both ligand exchange and ligand coupling. It also seems that the ligand exchange, ligand coupling and pseudorotation within the σ-sulfurane bearing carbon-centered ligands, take place very readily, the rates being within a close, small range, probably a few kcal mol^{-1}. These phenomena will have to be examined carefully in the future.

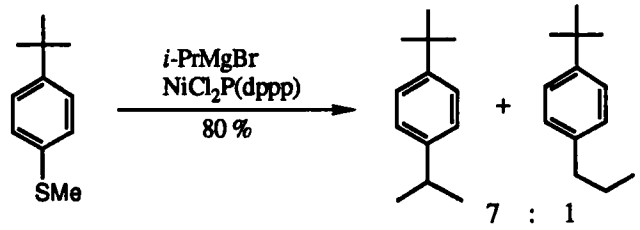
H. DESULFURIZATION WITH Ni AND OTHER METALLIC COMPLEXES

Earlier, Bonner et al. suggested, on the basis of their stereochemical observation of desulfurization of 2-phenyl-2-phenylthiopropioamide with Raney Ni in refluxing ethanol to result in the formation of a complete racemic mixture of the sulfide, as shown below, that the desulfurization is a free radical process.[110]

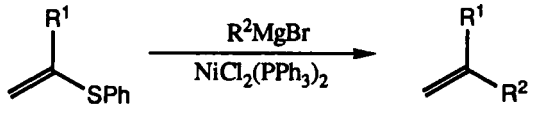


(optically active) (racemic mixture)

Recently Luh et al.[111] showed the following cross coupling reaction,[112] and many other similar cross-coupling reactions are in general stereospecific,[113-120] and complete retention of configuration has been observed.



The following reaction proceeded with a complete stereospecificity.[118]



The use of low-valent metal complex hydrides, i. e., Cp_2Ni or $NiBr_2(PPhe_3)_2$+$LiAlH_4$ is known to function similarly. $W(CO)_6$/PhCl is also known to desulfurize similarly, as in the reaction with $CuCl_2$.[111] Although no detailed mechanistic study has been carried out on these reactions, there is a possibility that all these are ligand coupling reactions. Further investigation is desired.

I. MISCELLANEOUS

Sulfuric acid is a cheap and very common reagent. It is a highly polar solvent, the dielectric constant being 120 as compared to 80 of H_2O, while its melting point is quite high, ca. 11 °C as compared to water, 0 °C. Sulfuric acid can dissolve many compounds, both organic and inorganic, and is known to fall in Mercury as the rain on our Earth. Much work has been carried out on the chemical behavior of sulfuric acid but always remained to be done much more in the future.

Similarly, sulfur is also a good solvent. Some works have been carried out on the reactions in a mixture of elemental sulfur and ammonia and amines, which usually generates a strong nucleophiles, recently by Sato et al., as shown earlier. However, much works can be done with the use of elemental surfur and elemental sulfur in ammonia or amines. Earth is known to be a rather exceptionally scant in the source of sulfur. Other planets and the universe are told to have much more sulfur sources. For exploring the universe, we should know much more sulfur chemistry.

Many polysulfides are known. Can we prepare polysulfones, $-(SO_2)_n-$, polysulfonediimines, $-(S(NH)_2)_n-$, polysulfoximines, $-(SO(NH))_n-$, and polysulfonium ylides, $-(S(CR_2)(CR'_2))_n-$? Are these stable?

In the last, but not the least, biochemistry on sulfur-centered

compounds, not alone elemental sulfur, has just started, but we should realize the enormous depth of the field. Some books are already made available, but much are hidden unexplored. All the significant discoveries have been to be done by those of the future generations.

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